Structure of {2,6-Bis[(dimethylamino)methyl]phenyl}dichloroiron(III), [Fe(C₁₂H₁₉N₂)Cl₂]

By A. de Koster, J. A. Kanters* and A. L. Spek

Vakgroep Algemene Chemie, Afdeling Kristal- en Structuurchemie, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

and A. A. H. van der Zeijden, G. van Koten and K. Vrieze

Anorganisch Chemisch Laboratorium, University of Amsterdam, J. H. van 't Hoff Instituut, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Abstract. $M_r = 318 \cdot 05$, monoclinic, $P2_1/n$, $a = 9 \cdot 0745$ (9), $b = 12 \cdot 2447$ (6), $c = 13 \cdot 5527$ (11) Å, $\beta = 99 \cdot 334$ (8)°, $V = 1486 \cdot 0$ (2) Å³, $Z = 4$, $D_x = 1 \cdot 422$ g cm⁻³, Mo $K\alpha$, $\lambda = 0 \cdot 71069$ Å, $\mu = 13 \cdot 8$ cm⁻¹, $F(000) = 660$, $T = 295$ K, $R = 0 \cdot 0294$ for 2553 observed reflections $[I > 2 \cdot 5\sigma(I)]$. The molecule represents a true organo-iron(III) compound. It has a square-pyramidal configuration around Fe, having C(1), N(1), N(2) and Cl(2) in the basal plane and Cl(1) in an axial position. The molecule has almost perfect mirror symmetry relative to the least-squares plane through Fe, Cl(1), Cl(2) and C(1) of the phenyl ring. One of the Cl atoms has three short Cl···H—C intermolecular contacts.

Introduction. Relatively little is known about the structures of (paramagnetic) organometallic compounds having a σ metal—carbon bond. Intramolecular coordination may have a considerable stabilizing effect on such complexes (Jastrzebski, Knaap & van Koten, 1983, and references cited therein).

In the course of investigations on the terdentate anionic ligand $o,o'\text{-}(Me_2NCH_2)_2C_6H_3$ we recently reported the crystal structures of $[Ni^{III}\{C_6H_3\text{-}(CH_2NMe_2)_2\text{-}o,o'\}I_2]$ (Grove, van Koten, Zoet, Murrall & Welch, 1983) and of $[Ni^{II}\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}\text{-}(CHO_2)]$ (Grove, van Koten, Ubbels, Zoet & Spek, 1984). In extending this research to the earlier transition metals we now report structural features of the newly synthesized 15-electron complex $[Fe^{III}\{C_6H_3\text{-}(CH_2NMe_2)_2\text{-}o,o'\}Cl_2]$.

Experimental. The very air-sensitive title compound was prepared from a reaction between $Li\{C_6H_3(CH_2\text{-}NMe_2)_2\text{-}o,o'\}$ and anhydrous $FeCl_3$ in benzene at room temperature. Crystals suitable for X-ray diffraction work were grown by slowly distilling pentane in a saturated solution of $Fe\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}Cl_2$ in benzene.

Dark-brown prismatic crystal $0 \cdot 45 \times 0 \cdot 47 \times 0 \cdot 95$ mm, sealed in a Lindemann-glass capillary under nitrogen. Enraf–Nonius CAD-4F diffractometer, Zr-filtered Mo $K\alpha$ radiation. Cell constants from angular setting of 12 reflections with θ range $11 \cdot 5$–$13 \cdot 5°$, space group $P2_1/n$ from systematic absences $h0l$ $(h + l \neq 2n)$ and $0k0$ $(k \neq 2n)$; standard deviations of lattice parameters calculated according to de Boer & Duisenberg (1984). Intensity data for 7489 reflections in one half of the reflection sphere; $0 \leq h \leq 11$, $-15 \leq k \leq 15$, $-17 \leq l \leq 17$; $\theta_{max} = 27 \cdot 5°$; ω–2θ scan mode; scan width $(0 \cdot 60 + 0 \cdot 35 \tan\theta)°$; horizontal and vertical apertures $3 \cdot 0$ and $4 \cdot 0$ mm respectively; scan speed selected to obtain $\sigma(I)/I < 1\%$ within a max. measurement time of 60 s/reflection. Intensities of three standard reflections $[103$ $(\sigma = 0 \cdot 7\%)$, $1\bar{3}2$ $(\sigma = 0 \cdot 9\%)$, 112 $(\sigma = 0 \cdot 4\%)]$ checked every hour. A linear decrease of about 25% was observed over a period of 11 h. Data were corrected for this decay, and for Lorentz and polarization effects and averaged $(R_{int} = 0 \cdot 049)$ resulting in 2553 observed reflections with $I > 2 \cdot 5\sigma(I)$. As a ψ scan of the 400 reflection showed an intensity variation $< 6\%$, no correction for absorption was applied. Structure solved by Patterson (Fe and Cl atoms) and subsequent Fourier methods. All H atoms located in a difference map. Weighted full-matrix least-squares refinement on F of 230 parameters with anisotropic non-H atoms and isotropic H's resulted in $R = 0 \cdot 0294$ and $wR = 0 \cdot 0422$, with $w^{-1} = \sigma^2(F_o) + 0 \cdot 001 |F_o|^2$ and $S = 1 \cdot 068$. Average and max. Δ/σ ratios $0 \cdot 028$ and $0 \cdot 133$ respectively; min. and max. residual densities $-0 \cdot 20$ and $0 \cdot 42$ e Å⁻³. No correction for secondary extinction. Scattering factors from *International Tables for X-ray Crystallography* (1974); anomalous-dispersion corrections from Cromer & Liberman (1970). All computations performed with *SHELX*76 (Sheldrick, 1976) and *EUCLID* (Spek, 1982) on the CDC Cyber 175 of the University of Utrecht.

Discussion. Fractional atomic coordinates are given in Table 1, the molecular structure with atom numbering

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* To whom correspondence should be addressed.

Table 1. *Atomic coordinates and equivalent isotropic temperature factors with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{eq}(\text{Å}^2)$
Fe(1)	−0·00403 (5)	0·12755 (5)	0·24939 (5)	0·0359 (1)
Cl(1)	0·0783 (1)	0·27389 (5)	0·34381 (5)	0·0570 (2)
Cl(2)	−0·2039 (1)	0·0600 (1)	0·3184 (1)	0·0620 (2)
N(1)	0·1393 (2)	−0·0014 (1)	0·3028 (1)	0·0501 (6)
N(2)	−0·1400 (2)	0·1870 (1)	0·1217 (1)	0·0436 (5)
C(1)	0·1381 (2)	0·1344 (2)	0·1572 (1)	0·0412 (6)
C(2)	0·2722 (3)	0·0812 (2)	0·1828 (2)	0·0489 (7)
C(3)	0·3778 (3)	0·0879 (3)	0·1192 (2)	0·067 (1)
C(4)	0·3437 (4)	0·1482 (3)	0·0330 (3)	0·075 (1)
C(5)	0·2097 (4)	0·2011 (2)	0·0068 (2)	0·067 (1)
C(6)	0·1014 (3)	0·1946 (2)	0·0704 (2)	0·0490 (7)
C(7)	0·2923 (3)	0·0238 (2)	0·2814 (2)	0·0607 (8)
C(8)	−0·0464 (3)	0·2487 (2)	0·0593 (2)	0·0562 (8)
C(9)	0·0841 (4)	−0·1023 (2)	0·2497 (2)	0·063 (1)
C(10)	0·1465 (5)	−0·0178 (3)	0·4127 (2)	0·079 (1)
C(11)	−0·2059 (3)	0·0900 (2)	0·0644 (2)	0·0526 (8)
C(12)	−0·2636 (4)	0·2572 (3)	0·1453 (3)	0·065 (1)

Fig. 1. View of the molecule with the adopted numbering scheme.

is shown in Fig. 1 and relevant bond distances and angles are listed in Table 2.* The crystal structure consists of discrete monomeric units, the packing of which is presented in Fig. 2. The fivefold coordination around the Fe atom can be described as a square pyramid with Fe displaced 0·517 (2) Å out of the basal plane defined by C(1), N(1), N(2) and Cl(2) towards apical Cl(1). Apart from slight deviations the complex is highly symmetrical with respect to the plane defined by Fe, Cl(1), Cl(2) and C(1). The phenyl ring is almost perpendicular [88·9 (1)°] to this plane. There are three short intermolecular Cl···H—C hydrogen-bond-type contacts between different molecules, all involving Cl(1) (Table 3). The angles between these Cl···H contacts are 62·0 (9), 89·2 (8) and 109·4 (8)°.

The molecular structure and crystal packing of the title compound resemble those of the analogous Ni^III complex [Ni{C₆H₃(CH₂NMe₂)₂-o,o'}I₂] (Grove, van Koten, Zoet, Murrall & Welch, 1983). Notable differences are (i) the X—M—C bond angles [NiI₂: 88·2 (2) and 168·8 (2)°; FeCl₂: 97·89 (7) and 156·89 (8)°], (ii) the N—M—N bond angle [NiI₂: 152·0 (2)°; FeCl₂: 142·97 (5)°] and (iii) the M—X bond lengths: in the Ni complex these distances are nearly equal [2·613 (1) and 2·627 (1) Å] whereas in the Fe complex there is a significant difference [axial: 2·258 (1) and equatorial: 2·324 (1) Å], while the X—M—X angles are very similar [103·0 (1) and 105·22 (5)° respectively].

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and geometry, and details of least-squares molecular planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42076 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
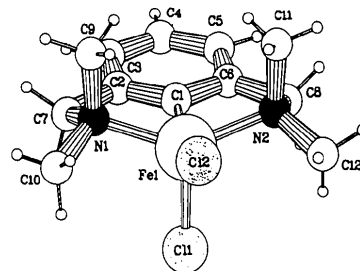
Table 2. *Bond distances (Å) and angles (°)*

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Fe(1)—Cl(1)	2·2575 (9)	N(2)—C(12)	1·488 (4)
Fe(1)—Cl(2)	2·324 (1)	C(1)—C(2)	1·375 (3)
Fe(1)—N(1)	2·098 (2)	C(1)—C(6)	1·383 (3)
Fe(1)—N(2)	2·087 (2)	C(2)—C(3)	1·391 (4)
Fe(1)—C(1)	1·937 (2)	C(2)—C(7)	1·494 (4)
N(1)—C(7)	1·496 (3)	C(3)—C(4)	1·375 (5)
N(1)—C(9)	1·475 (3)	C(4)—C(5)	1·373 (5)
N(1)—C(10)	1·494 (3)	C(5)—C(6)	1·411 (4)
N(2)—C(8)	1·497 (3)	C(6)—C(8)	1·481 (4)
N(2)—C(11)	1·489 (3)		
Cl(1)—Fe(1)—Cl(2)	105·22 (5)	Fe(1)—N(2)—C(12)	112·8 (2)
Cl(1)—Fe(1)—N(1)	105·81 (5)	C(8)—N(2)—C(11)	108·9 (2)
Cl(1)—Fe(1)—N(2)	106·86 (5)	C(8)—N(2)—C(12)	110·3 (2)
Cl(1)—Fe(1)—C(1)	97·89 (7)	C(11)—N(2)—C(12)	108·7 (2)
Cl(2)—Fe(1)—N(1)	94·25 (6)	Fe(1)—C(1)—C(2)	118·1 (1)
Cl(2)—Fe(1)—N(2)	93·58 (6)	Fe(1)—C(1)—C(6)	118·6 (2)
Cl(2)—Fe(1)—C(1)	156·89 (8)	C(2)—C(1)—C(6)	123·3 (2)
N(1)—Fe(1)—N(2)	142·98 (6)	C(1)—C(2)—C(3)	119·1 (2)
N(1)—Fe(1)—C(1)	79·33 (8)	C(1)—C(2)—C(7)	115·0 (2)
N(2)—Fe(1)—C(1)	79·41 (7)	C(3)—C(2)—C(7)	125·8 (3)
Fe(1)—N(1)—C(7)	108·7 (1)	C(2)—C(3)—C(4)	118·4 (3)
Fe(1)—N(1)—C(9)	108·6 (1)	C(3)—C(4)—C(5)	122·8 (3)
Fe(1)—N(1)—C(10)	111·7 (2)	C(4)—C(5)—C(6)	119·4 (3)
C(7)—N(1)—C(9)	109·3 (2)	C(1)—C(6)—C(5)	117·0 (2)
C(7)—N(1)—C(10)	109·2 (2)	C(1)—C(6)—C(8)	114·4 (2)
C(9)—N(1)—C(10)	109·3 (2)	C(5)—C(6)—C(8)	128·5 (3)
Fe(1)—N(2)—C(8)	109·4 (1)	N(1)—C(7)—C(2)	106·7 (2)
Fe(1)—N(2)—C(11)	106·7 (1)	N(2)—C(8)—C(6)	107·7 (2)
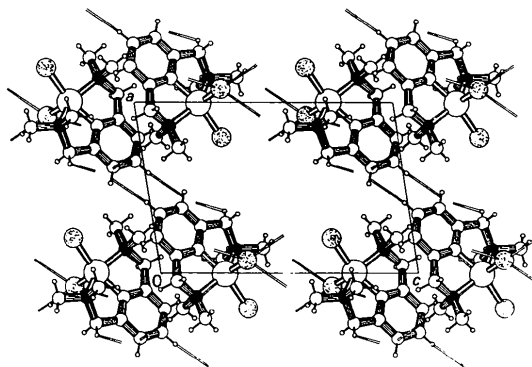
Fig. 2. Projection of the structure down **b**, illustrating the packing and the short Cl···H contacts. Only one layer is shown; a second layer may be superimposed with the twofold screw axis at ¼, 0, ¼. N atoms are represented by black spheres and Cl atoms by stippled spheres.

Table 3. *Short intermolecular contacts*

$A \cdots H-D$	$D-H(\text{Å})$	$A \cdots H(\text{Å})$	$A \cdots H-D(°)$
Cl(1)⋯H(10ⁱ)—C(4ⁱ)	0·95 (3)	2·80 (3)	161 (2)
Cl(1)⋯H(15ⁱⁱ)—C(11ⁱⁱ)	0·94 (3)	2·77 (3)	168 (2)
Cl(1)⋯H(7ⁱⁱⁱ)—C(7ⁱⁱⁱ)	1·04 (3)	2·93 (3)	139 (2)

Symmetry code: (i) $-\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$; (ii) $\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$; (iii) $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$.

These differences are a reflection of the difference in electronic configuration of the metal centres. The Ni^{III} complex has a low-spin ($S = \frac{1}{2}$) d^7 environment. ESR spectra of the Fe^{III} complex at low (147 K) or ambient temperatures in toluene are indicative (Hollis Wickman, Klein & Shirley, 1965; Niarchos, Kostikas, Simopoulos, Coucouvanis, Piltingsrud & Coffman, 1978; Toney, ter Haar, Savrin, Gold, Hatfield & Sangaiah, 1984) of an intermediate-spin ($S = \frac{3}{2}$) d^5 electronic distribution (a strong signal at $g_\perp = 4·14$ and a weak signal at $g_\parallel = 2·00$). However, the commonly encountered admixture of the high-spin state ($S = \frac{5}{2}$) may cause a destabilization of the $d_{x^2-y^2}$ orbital and hence some weakening and distortion of bonds in the equatorial plane.

Finally it should be mentioned that a similar attempt to prepare the ruthenium analogue failed.

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Dicarbonylchloro(η^5-cyclopentadienyl)eisen(II), [Fe(η^5-C₅H₅)(CO)₂Cl]

VON KLAUS-JOACHIM JENS UND ERWIN WEISS*

Institut für Anorganische und Angewandte Chemie der Universität Hamburg, Martin-Luther-King-Platz 6, D-2000 Hamburg 13, Federal Republic of Germany

Abstract. $M_r = 212·3$, orthorhombic, $P2_12_12_1$, $a = 5·964$ (2), $b = 10·963$ (5), $c = 12·354$ (7) Å, $V = 807·8$ Å³, $Z = 4$, $D_x = 1·748$ g cm⁻³, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 20·5$ cm⁻¹, $F(000) = 456$, $T = 298$ K, $wR = 0·038$ for 1051 reflexions. The title compound has a 'piano-stool' structure, *i.e.* the coordination geometry of the Fe can be regarded as a distorted octahedron with the η^5-C₅H₅ group occupying three coordination sites. Atom distances and angles correspond to this structure type.

Einleitung. Bei der Umsetzung von K[(η^5-C₅H₅)-Fe(CO)₂] mit SOCl₂ erhielten wir unerwartet die Titelverbindung. Sie wurde bereits 1955 aus [(η^5-C₅H₅)Fe(CO)₂]₂ und HCl/CHCl₃ dargestellt (Piper, Cotton & Wilkinson, 1955), jedoch noch nicht röntgenographisch untersucht. In struktureller Beziehung hierzu steht die Verbindung [(η^5-C₅H₅)-Fe(CO)₂Cl]₂.SbCl₃ (Einstein & MacGregor 1974).

Experimentelles. 4,5 g (18 mmol) K[(C₅H₅)Fe(CO)₂] werden in 150 ml THF gelöst und in einem Eisbad gekühlt. Anschliessend werden 1,45 ml (20 mmol) Thionylchlorid, gelöst in 20 ml THF, hinzugetropft. Danach wird 1 h bei 293 K gerührt. Nach Abfiltrieren und Abzug des Lösungsmittels wird in Toluol aufgenommen und an Kieselgel chromatographiert (Säule: Länge 20 cm, Durchmesser 6 cm). Mit Toluol

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* Korrespondenzautor.